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Colloids and Surfaces A: Physicochemical and Engineering Aspects

Nanoscale conversion of chlorapatite into hydroxyapatite using ultrasound irradiation

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HIGHLIGHTS

- Chlorapatite nanoparticles are precipitated from a HCl solution of phosphate rock.
- Sonication allows the topotactic conversion of chlorapatite into hydroxyapatite.
- Undersaturated conditions lead to particle size reduction and not to amorphization.
- This method provides a fast route to well-defined hydroxyapatite nanocrystals.

GRAPHICAL ABSTRACT
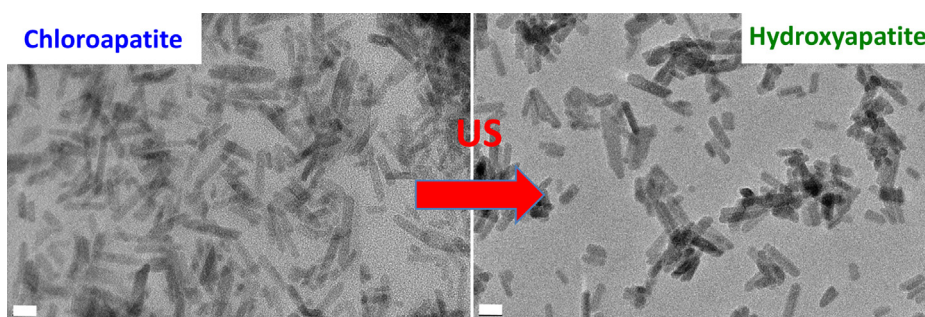
ARTICLE INFO

ABSTRACT

The ultrasound-assisted conversion of chlorapatite nanoparticles obtained from a natural phosphate rock into hydroxyapatite nanocrystals was achieved within one hour. The process had no significant impact on particle crystallinity but led to a significant decrease of the colloidal size. Similar variations were obtained for hydroxyapatite nanoparticles treated in the same conditions, suggesting that these variations are not due to the compositional modification. Analyses of the solubility properties of the two phases and of the ionic contents of the reaction medium suggest that the undersaturated conditions of the reaction and the cavitation phenomena favor surface exchange and erosion mechanisms over bulk amorphization.

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1. Introduction

Natural phosphates are one of the major reservoirs of both phosphorus and calcium in the Earth's crust [1]. Fluoroapatite ($Ca_{10}(PO_4)_6F_2$), and its carbonated form francolite, is the main component of Moroccan natural phosphates [2–4]. Among other applications, the cation-exchange properties of phosphocalcic apatites as well as their rich surface chemistry make them valuable materials as sorbents for water remediation [5–8]. However, natural apatites exhibit low specific areas that limit their sorption capacity [9–11]. Therefore many physical and chemical routes have been developed to obtain phosphocalcic apatites as high surface area powders from inorganic salts [12]. Of particular interest here are sonochemistry routes that allow control of the particle size and crystallinity through the modulation of irradiation power and duration [13–21]. As a more sustainable alternative, a process allowing for the conversion of natural phosphate into porous hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) was recently described [22,23]. The procedure involves the dissolution of the natural ore in nitric acid, filtration

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Table 1
Chemical analysis of the phosphate rock used in this study [4].

% Ca	% P	% F	%Si	%S	%Na
37.84	15.03	2.84	1.78	0.78	0.79

of the remaining minerals (mainly quartz) and reprecipitation by neutralization.

Although this approach has the benefits of using raw materials available in large quantity and being performed in purely aqueous conditions, the use of nitric acid at a large scale is associated with explosive hazards related to its strong oxidizing power. In this study, we examined hydrochloric acid as an alternative dissolution medium. The precipitated material was a nanopowder of chlorapatite ($Ca_{10}(PO_4)_6Cl_2$), whose reactivity is lower than hydroxyapatite due to the key role of OH^- in its surface properties. Topotactic, *i.e.* shape preserving, conversion of chlorapatite and other phosphocalcic apatite into hydroxyapatite has already been described in hydrothermal conditions from well-crystallized powders [24,25]. These approaches required strong alkalinity (KOH, 6.25 M), high temperatures (>300 °C) and relatively long reaction times (>12 h) but allowed for conversion of large crystals (several mm). Alternatively, for nanoscale particles with high interfacial reactivity and easy dispersion, topotactic transformations of calcium phosphates using ultrasound irradiation appears as a suitable and fast method [26,27]. On this basis, the effect of sonication on the topotactic transformation of chloroapatite nanocrystals into hydroxyapatite was demonstrated and the mechanisms by which the conversion can be influenced by ultrasound irradiation are discussed. In particular, the key role of undersatured conditions on the ultrasound-induced transformation is evidenced. These results demonstrate that the structural conversion can be achieved without particle amorphization but with size reduction, offering a simple and original method to obtain hydroxyapatite nanoparticles with tailored crystallinity and dimensions.

2. Materials and methods

2.1. Materials

The phosphate rock sample used was from the Bengurir region (Morocco). The sample was washed and then sieved to give a −400/+100 μm size fraction using ASTM Standard sieves, this grain size being optimum for efficient dissolution. As reported earlier [4], it consists of a mixture of francolite and quartz (2.5 wt%) and its composition in major mineral elements is provided in Table 1.

2.2. Synthesis

The conversion of the natural ore into nanosized powders was performed according to a previously described procedure [23]. Dissolution of the phosphate rock was carried out in a 1 L open glass reactor with a spherical bottom at a rate of 200 rpm. For each experiment, the temperature was set to 25 °C. The phosphate rock (20 g) was first dissolved in 80 mL of deionized water supplemented with 20 mL of concentrated hydrochloric acid (37%) or nitric acid (65%) to obtain the solvated Ca^{2+} and hydrogenophosphate species. Insoluble matter, mainly quartz, was then separated by filtration. The remaining solution was neutralized using 100 mL of a concentrated NH_4OH solution (25%). The pH value of the precipitation reaction was maintained at pH 10 to avoid the formation of other non-apatitic calcium phosphates. The resulting powder was recovered by filtration and either washed several times with deionized water or re-dispersed in 100 mL deionized water under stirring for 30 min and then placed in an ultrasonic water bath (200 W, 35 kHz) for 1 h. The resulting products were recovered by filtration and thoroughly
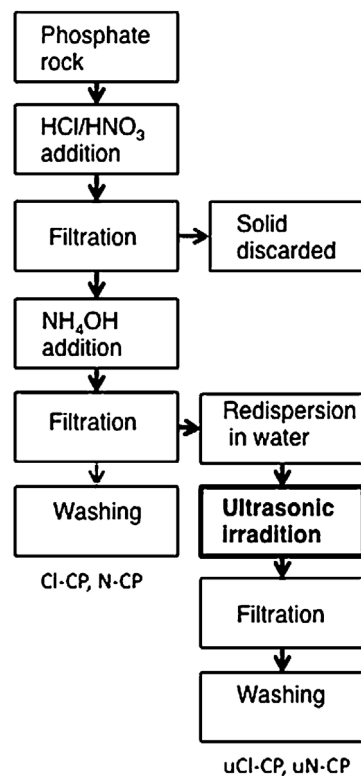

Fig. 1. Flow diagram of the preparation of nanosized apatite samples.

washed with water. Both set of samples were dried overnight at 100 °C. The precipitated samples are noted Cl-CP and N-CP according to the inorganic acid (HCl and HNO_3) used for dissolution; uCl-CP and uN-CP correspond to the powders obtained from sonication. Further heating of the samples was performed at 800 °C. The overall flow diagram of the process is summarized in Fig. 1.

2.3. Characterization

The crystalline phases were identified using a powder X-ray diffractometer (XRD) (Philips PW131 diffractometer) using the CuKα radiation. Infrared spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} on a Bruker IFS 66v Fourier transform spectrometer using KBr pellets. Particles were imaged using Transmission Electron Microscopy (TEM) on a TECNAÏ G2 instrument. Calcium and phosphorus content of the powders were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICPS-7500, Shimadzu, Japan). Chloride content was determined using the Mohr method. The N_2 adsorption-desorption isotherms for dried powders were obtained by multi-point N_2-gas adsorption-desorption experiments at 77 K using a Micromeritics ASAP 2010 instrument. The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method using adsorption data in the relative pressure range from 0.05 to 0.25 whereas the pore size and volume were estimated using the Barret-Joyner-Halenda (BJH) approximation.

3. Results

The X-Ray diffractograms of non-sonicated Cl-CP and N-CP dried at 100 °C and heated at 800 °C are shown in Fig. 2a. The dried Cl-CP and N-CP samples exhibit a series of very similar low intensity peaks but differ from a multi-component signal in the $2\theta = 31$–$34°$ range for the former and 32–$35°$ domain for the latter. After heating at 800 °C much narrower diffraction peaks are obtained allowing